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RPPR Final Report
as of 12-Oct-2017

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Proposal Number: 68478EGRIP

Agreement Number: W911NF-16-1-0393

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Final Report for Period Beginning 15-Jul-2016 and Ending 14-Jul-2017

Title: Diagnostic System for Decomposition Studies of Energetic Materials

Begin Performance Period: 15-Jul-2016

End Performance Period: 14-Jul-2017

Report Term: 0-Other

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 0

STEM Participants: 2

Major Goals: The major goal of this project is to purchase and install a new Fourier transform infrared spectrometer, as this is an equipment grant. The spectrometer is to be interfaced with an existing confined rapid thermolysis system, which has been designed and constructed under previous ARO support. In this thermolysis system, small amounts of energetic materials are used to provide data and improved understanding in modeling of reactions with quantum mechanics calculations.

Accomplishments: The spectrometer has been purchased, delivered and installed. All necessary changes have been made to the optical layout to accommodate the new spectrometer.

Training Opportunities: There has been training of graduate students in the use of this piece of equipment.

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Stefan Thynell

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

RPPR Final Report
as of 12-Oct-2017

Abstract

The funds from this equipment proposal were used to update a species diagnostic system used in thermolysis of energetic materials. Specifically, the funds were used to purchase a Fourier transform infrared (FTIR) spectrometer manufactured by Bruker (Vertex 80), which acquires transmittance spectra of the evolved gaseous species at speeds ranging from slow to 20 spectra per second at 2 cm^{-1} spectral resolution. The FTIR spectrometer is primarily interfaced with an existing confined rapid thermolysis system of either liquid or solid samples in milligram quantities, allowing heating at rates of $2,000\text{K/s}$ and applied pressures to $1,000\text{ psig}$. The system is used in two existing projects. In the first ARO-sponsored project, it is used to identify species from slow and rapid thermolysis of RDX and mixtures of RDX with a high-nitrogen compound. In the second project funded by AFOSR, the diagnostic system is used to identify species evolution of energetic materials containing catalytic nanoparticles. These species measurements provide guidance to a quantum mechanics investigation, in which the transition states and reaction pathways are sought. The overall objective for these combined experimental studies and quantum mechanics investigations is to identify the relevant reaction channels at high heating rates and to develop reaction mechanisms, which can be used in computational fluid dynamic studies of ignition and combustion of solid and liquid propellants used in propulsive devices.

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Cost and Technical Specifications of the Purchased FTIR Spectrometer

Table 1 lists the components and their costs of the purchased FTIR spectrometer. Table 2 lists the technical details of the purchased Vertex 80 FTIR spectrometer, and Fig. 1 shows the internal optical layout of the FTIR spectrometer.

Table 1. Components and Costs of the Bruker model Vertex 80 FTIR spectrometer, and other required parts as listed below. (Mr. Dana Kelley, Bruker Optics Inc., 19 Fortune Drive, Billerica, MA 01821, (978) 439-9899, dana.kelley@bruker.com)

Item	Material/Description	Quant.	Unit price	Amount
1	V80-Infrared Fourier Spectrometer VERTEX 80 Powerful purge FT-IR spectrometer covering spectral range from $8,000$ to 350cm^{-1} . The following components are included in the basic system price: MIR-KBr beam splitter (T303/8) Room temperature DLaTGS detector (D301/B), High power IR source, Aperture wheel with 12 positions. Validation wheel with 6 positions. Automatic sample compartment shutters. OPUS/IR software package. Rapid Scan with >110 spectra/sec at 16 cm^{-1} resolution. External measurement channels.	1	\$72,015.00	\$72,015.00
2	W105/H-E Detector adaption, external; consisting of base with off axis parabolic mirror ($f=43\text{mm}$), dovetail mount for detector with integrated ADC and electrical connection to the spectrometer (3m)	1	\$2,619.00	\$2,619.00
3	A171/Z-R	1	\$2,754.00	\$2,754.00

	Adaption set for connection of external accessories to the right side of the spectrometer. The set contains computer controlled beam steering mirror, window and flange.			
4	E516/B Digital I/O for the synchronization of external experiments in the Rapid-Scan and TRS mode, 1bit in, 1bit out, opto-is TTL)for internal or external start trigger of the measurement.	1	\$1,085.40	\$1,085.40
5	D126 Pumping valve for N ₂ detector-dewars	1	\$1,185.30	\$1,185.30
6	D315/BF MCT detector, medium band, liquid N ₂ cooled. Spectral range: 12,000-600cm ⁻¹ , D*: >2×10 ¹⁰ cm Hz ^{1/2} /W, Hold time typically 8h; Integrated amp. and digitizing electronics.	1	\$9,841.50	\$9,841.50
7	E550/A Electronic adaption for connecting up to two detectors	1	\$1,044.90	\$1,044.90
8	I10290 Flexible metal hose for vacuum pump adapter D126 including NW25 flange	1	\$940.95	\$940.95
9	S129/8 Rapid scan option for more than 110 spectra/sec at a spectral resolution of 16 cm ⁻¹ . Includes extended scanning speed range up to 320kHz. Required: D31x/B MCT or an alternative fast detector; F321 or F321-H Optical Filter; OPUS/3D evaluation Software	1	\$2,754.00	\$2,754.00
10	W105/Z Unit for selecting an additional IR detector in position 2 (without detector, not compatible with W105/Z2)	1	\$3,483.00	\$3,483.00
11	S316/7 Air flow regulator for purge. Requires supply of dry air or nitrogen	1	\$592.65	\$592.65
12	F321 Optical filter, LWP <3,861cm ⁻¹	1	\$934.20	\$934.20
13	O/IR+ OPUS/IR, FT-IR Spectroscopy Software Package	1	\$0.00	\$0.00
14	O/3D-N OPUS/3D, Software package for 3D data processing, evaluation and visualization	1	\$1,539.00	\$1,539.00
15	O/SR-NP OPUS/SEARCH	1	\$0.00	\$0.00
16	CS81/26+ Data System, Microtower "Intel" processor, >3GHz, 4GB RAM 1TB HDU or better, DVD, 21.5" TFT display. Ports: USB 3.0, 2.0 (10x), PS/2(2), RJ-45 Network(2), RS232, VGA, DisplayPort (2), line in, line out, PCIe	1	\$1,906.20	\$1,906.20

	x16(2), PCIe x1(2). Operating System: Windows 7 Ultimate or better. (only available with order of spectrometer)			
17	S950+ Installation on-site included in the price of the system (including travel charges, inland)	-	\$0.00	\$0.00
	Total Price			\$102,695.10
	Academic discount (10%)			-\$10,269.51
18	Custom built frame and parabolic/flat mirrors for external detector by Bruker	1	\$1446.94	\$1,446.94
19	Dessicator and dessicant to store beam splitter in a dry environment from Cole Parmer	1	\$631.80	\$631.80
20	Lexan for constructing purge gas box for external detector purchased from McMaster-Carr	1	\$371.12	\$371.12
21	Backup and removable hard drive from Newegg.com	1	\$124.55	\$124.55
	Total cost for the FTIR spectrometer			\$95,000.00

Table 2. Technical details of the Vertex 80 FTIR spectrometer by Bruker.

Item	Property
Spectral ranges	8,000 to 350cm ⁻¹ standard, with KBr beamsplitter, DLaTGS detector and MIR source
Spectral range options	Far IR/THz: 680 to 10cm ⁻¹ , Near IR: 15,500 to 4,000cm ⁻¹ Visible: 25,000 to 9,000cm ⁻¹ , Ultraviolet: 50,000 to 25,000cm ⁻¹
Beamsplitter options	KBr (broadband): 10,000 to 380cm ⁻¹ CaF ₂ -NIR: 15,500 to 1,200cm ⁻¹ , CaF ₂ -UV/VIS/NIR: 50,000 to 4,000cm ⁻¹ Multilayer far IR: 680 to 30cm ⁻¹ , Mylar 23µm: 120 to 30cm ⁻¹ , Mylar 50µm: 60 to 10cm ⁻¹ ; Beamsplitters are easily exchangeable and automatically aligned; Two storage positions inside optics bench are available
Source	Mid and far IR ceramic source, air cooled
Source options	Internal near IR/Visible tungsten source, air cooled; External water cooled far IR Mercury arc lamp, high power ceramic and tungsten sources; External Deuterium-UV lamp, air cooled
Detectors	DigiTect* detector system, standard high sensitivity DLaTGS - detector
Detector options	DLaTGS with CsI and far IR DTGS with PE window LN ₂ cooled MCT's (photo conductive and photovoltaic) LN ₂ cooled InSb and MCT/InSb sandwich detectors InGaAs-, Si- and GaP-diodes; Far IR/THz liquid at He cooled bolometer detectors
Spectral resolution	Better than 0.2cm ⁻¹ , optional better than 0.07cm ⁻¹
Resolving power	v/Δv better than 300,000:1 (for vis spectral range only)
Wavenumber accuracy	Better than 0.01cm ⁻¹ at 2,000cm ⁻¹
Photometric accuracy	Better than 0.07% T
Signal-to-Noise	5 sec sample, 5 sec reference: >7,500:1 (<5.8×10 ⁻⁵ AU noise) peak-to-

	peak at $2,000\text{cm}^{-1}$, 4cm^{-1} spectral resolution and standard optical components
Signal-to-Noise, typical	5 sec: 10,000:1 (4.4×10^{-5} AU noise) peak-to-peak 1 min: 50,000:1 (8.6×10^{-6} AU noise) peak-to-peak
Interferometer	UltraScan linear air bearing scanner with True-Alignment
Aperture ratio	f/2.5, nominal beam diameter 40mm (1.57")
Scan Speed	12 velocities standard, 1.6 – 160kHz (1.0 – 100 mm/sec opd) Optional: 16 velocities, 1.6 – 320kHz (1.0 – 200 mm/sec opd)
Rapid Scan	>65 spectra/sec at 16cm^{-1} spectral resolution
Rapid Scan option	>100 spectra/sec at 16cm^{-1} spectral resolution
Step Scan option	5/10 nanoseconds temporal resolution using a dual channel transient recorder and fast detector
A/D converter	True 24 bit dynamic range for all scan velocities, dual channel data acquisition
Validation	Internal validation unit, 6 positions, certified standards optional
Aperture wheel	12 positions, fixed diameters, ranging from $250\mu\text{m}$ to 8mm
Optics bench	Sealed and purgable, automatic sample compartment shutters included
Flexibility & automation opt.	Two internal detector positions, each one compatible with LN_2 detector dewars, software selectable Two internal source positions, software selectable Five output ports at the right, front and left side of the optics bench, software selectable Two input ports at the right (uses aperture and optical filter wheels) and rear side of the optics bench, software selectable
Sample Compartment Size	$25.5(\text{W}) \times 27(\text{D}) \times 16(\text{H}) \text{ cm}$
Optics Bench Size	$84(\text{W}) \times 64(\text{D}) \times 27.5(\text{H}) \text{ cm}$
Weight	ca. 76 kg (basic configuration)
Power	100 - 240 VAC, 50 - 60Hz, 100W (without data station)
Computer Interface	Industry standard Ethernet connection, TCP/IP protocol
Software	Integrated OPUS easy to use, fully GLP and 21 CFR part 11 compliant software

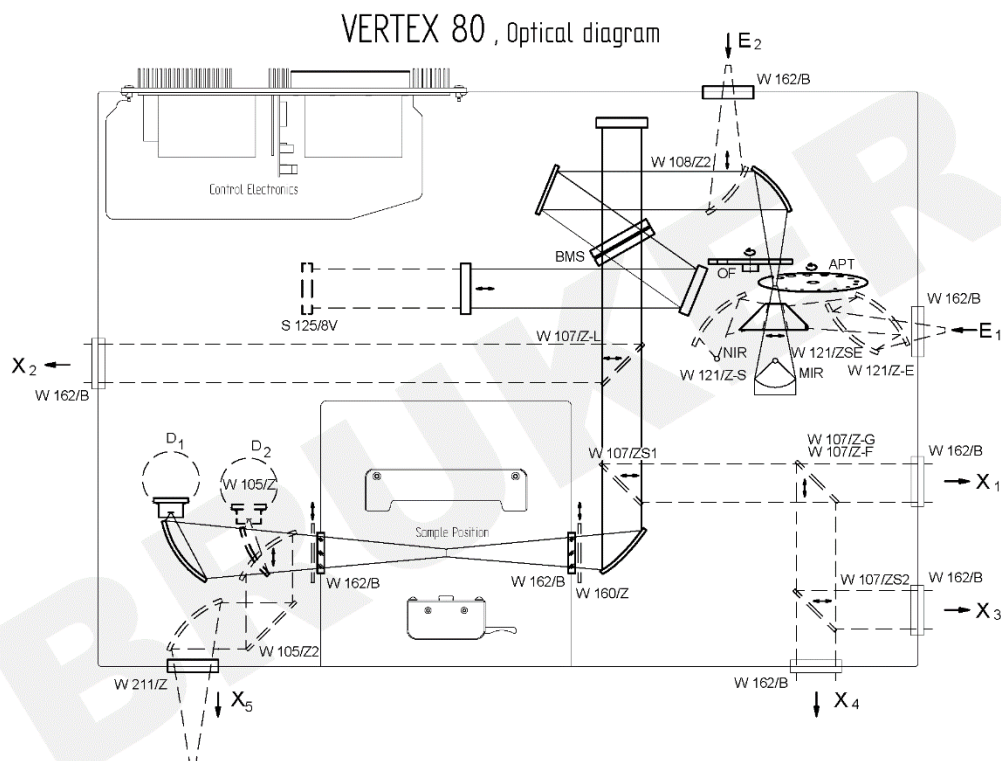


Figure 1. Optical diagram of the vertex 80 spectrometer. The setups for acquiring transmission spectra of gases from confined rapid thermolysis or pressed KBr samples are accessed via port X₁, whereas the gases from the TGA/DSC apparatus are accessed via port X₂. The W 107/x are electronically controlled flipper mirrors. Please note that the quotation contains part numbers that are different from in Fig. 1, due to part upgrades.

Sample of Results from Thermolysis Experiments

Experimental and Quantum Mechanics Investigations for the Development of a Liquid-phase Chemical Reaction Mechanism of RDX, ARO Grant # W911NF-15-1-0202 (PI: S. Thynell, Program Manager: Dr. R. Anthenien)

The primary objective of the research is to develop a detailed liquid-phase decomposition mechanism of RDX, which includes only elementary reactions. As part of this effort, the developed liquid-phase RDX mechanism will be used in an ignition and combustion code to predict the flame structure, burn rate and temperature sensitivity of the monopropellant. The liquid-phase RDX mechanism will also be integrated with a chemical kinetics mechanism of a burn-rate modifier, in order to examine the burning behavior of a pseudo-propellant. A liquid-phase decomposition mechanism of the burn-rate modifier, based on elementary chemical reactions, will also be formulated. The integration of these two ingredients will also require the identification of transition states for additional gas-phase, elementary reactions in the ignition and combustion model. In order to validate these developed mechanisms, it is very useful to have a wide range of thermal decomposition data available for validation. Currently a confined rapid thermolysis setup is used to identify species evolved. However, the corresponding temporal behavior of mass loss and heat release cannot be measured.

Figure 1 shows a sample of the results obtained. Clearly, the signal-to-noise ratio is excellent throughout the entire spectral range. It does, however, drop off near 600cm^{-1} , but that is expected. The weak absorbers CO and NO can clearly be seen: *P*-branch of CO at 2150 cm^{-1} , and the *P*-, *Q*- and *R*-branches of NO near 1850 cm^{-1} . The *R*-branch of CO is on top of the very strong *P*-branch of N_2O near $2,200\text{ cm}^{-1}$.

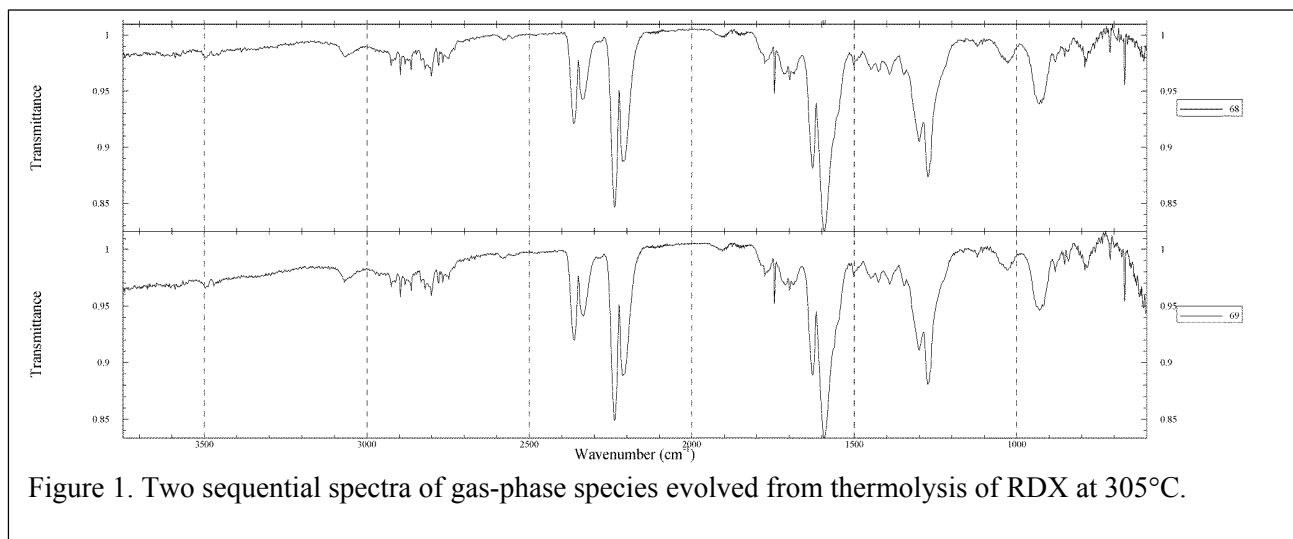


Figure 1. Two sequential spectra of gas-phase species evolved from thermolysis of RDX at 305°C .

MURI-Smart Functional Nanoenergetic Materials, AFOSR Grant # FA9550-13-1-0004 (PI: R. Yetter, Co-PI: S. Thynell, Program Manager: Dr. M. Birkan)

The proposer's objective in this program is to develop an understanding of the role of nanoparticles on the condensed-phase decomposition of energetic materials. The present focus is on AP and embedded nano-particles of Fe_2O_3 . The first step in such a study is to examine the decomposition of the oxidizer itself, which has been done using the previous spectrometer. The next step is formulate a mechanism of AP decomposition, which is currently under way. During the next year, experimental studies will be carried out using AP particles containing the iron oxide catalyst. We have a very limited amount of such particles, and most studies might be carried out using the combined apparatus of FTIR/TGA/DSC, which has been ordered and the TGA has been delivered. The interface between the spectrometer and the TGA has not yet been delivered, however.

Existing Research Capability is Maintained

The FTIR system will continue to provide a capability to study decomposition of energetic materials at high heating rates. Such capability is not available here on campus. The system, which utilizes a confined rapid thermolysis, allows the study of both solid and liquid samples, including fairly volatile liquid samples. The spectrometer is also used to examine the residue remaining on the aluminum foil after thermolysis, as well as the condensate from evaporation of decomposed products which is collected on room-temperature surface. In these two cases, a sample is mixed with potassium bromide (KBr) and transmission measurements are performed on pressed KBr pellets.

Current Projects

November 2012 - October 2018 (incl. 1 year no-cost extension), “MURI-Smart Functional Nanoenergetic Materials,” AFOSR Grant # FA9550-13-1-0004 (PI: R. Yetter, Co-PI: S. Thynell, Program Manager: Dr. M. Birkan), approx. \$750k/5 years.

May 1, 2015- April 30, 2020, “Experimental and Quantum Mechanics Investigations for the Development of a Liquid-phase Chemical Reaction Mechanism of RDX,” ARO Grant # W911NF-15-1-0202 (PI: S. Thynell, Program Manager: Dr. R. Anthenien), approx. \$980k/5 years.